

Article

Dissipation Kinetics and Dietary Risk Assessment of Boscalid Residues in Two Table-Grape Varieties Under Field Conditions

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Abstract: Grape cultivation is crucial due to its significant dietary benefits and the production of various byproducts. Fungicides, like boscalid, are frequently applied to protect grape crops from several disease, ensuring both yield and quality. However, the excessive or inappropriate application of boscalid may pose health risks to humans. Therefore, the objectives of this field study were (a) to assess the pre-harvest interval (PHI) and dissipation of boscalid in two table-grape varieties (Soultanina and Crimson) under field conditions and (b) evaluate the potential health risks associated with grape consumption for both adults and children. The residue of boscalid in the grapes was determined using a modified QuEChERS method coupled with a high-performance liquid chromatography diode array detector (HPLC–DAD). The dissipation of boscalid followed first- and second-order kinetics, with half-lives ranging from 3.32 to 6.42 days and PHIs from 8.11 to 10.90 days. The dietary risk assessment indicated that the early to mid-post application period could pose risks for both age groups, with children facing three times the risk of adults.

Keywords: fungicides; kinetic models; risk assessment; dietary exposure; table grapes



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1. Introduction

In terms of total production value, grapes (*Vitis vinifera* L.) rank as the top fruit globally, followed by oranges, apples, watermelons, bananas, and mangoes [1]. The consumption of grapes (*Vitis vinifera* L.) is growing rapidly, both for the fruit itself and its byproducts. Grape farming is important because of its outstanding dietary traits and the production of byproducts. Therefore, grapes and grape-based products, including wine, jam, juice, vinegar, raisins, and grape seed oil, are produced in increasing quantities each year [2,3]. These fruits have excellent nutritional profiles, are delicious, and are highly perishable. Because of their high fiber and folic acid content, the berries help lower blood cholesterol, body weight, and the risk of developing severe hypertension [4]. According to data from the FAO, grapes are grown on about 75,866 km² of agricultural land, with table grapes making up about 27% of the world's total grape production [5].

Fungicides are applied during grape cultivation in order to prevent diseases [6–8]. Throughout the ripening process, grapes face a significant risk of disease from various fungal species, which can reduce the quality and yield of the crop [5]. Several diseases

such as black rot (*Guignardia bidwellii*), botrytis rot (*Botrytis cinerea*), and downy mildew (*Plasmopara viticola*) can infect the fruit and aerial parts of plants [9].

Boscalid (CAS name: 2-chloro-N-(4'-chloro [1,1'-biphenyl]-2-yl)-3-pyridinecarboxamide), a carboxamide fungicide, was developed as an alternative to fungicides with a different mode of action. High-end specialty crops including fruits, vegetables, wine, and horticultural plants have greatly benefitted from boscalid's adaptability, broad-spectrum application, and environmentally friendly properties in managing a wide range of pathogenic fungi such as *Sclerotinia*, *Alternaria*, and *Botrytis* species [10,11]. Boscalid limits fungal respiration by inhibiting the particular binding sites associated with Krebs's cycle, which has a substantial suppressive impact on spore germination, resulting in an extremely efficient treatment for plant diseases [12]. Boscalid's low toxicity to birds and mammals has contributed to its widespread use for crop protection throughout the plant growing season since its market release in 2002 [13]. However, boscalid is not just selective for the organisms it targets. According to published research, it also affects human cells and non-target organisms including zebrafish and *Chlorella vulgaris*. Because of its apparent lack of specificity of action, this fungicide is hazardous to almost all living things, even though it has been categorized as moderately toxic to aquatic invertebrates and vertebrates [14–16]. Nevertheless, fungicide overuse or improper application may result to high pesticide residue levels on crops, potentially posing health risks to consumers [17,18].

Pesticides can cause cancer, birth defects, reproductive abnormalities, toxicity, and even death, among other negative health impacts; this is increasingly supported by epidemiological and molecular research [19]. The European Union (EU) and numerous other nations have set maximum residue limits (MRLs) for pesticides in agricultural goods in order to mitigate the possible hazards of pesticide residues. These limits aim to ensure that residues in food remain safe for human consumption, particularly since many people consume fruits and vegetables raw [20,21].

In practice, an MRL is determined as the amount of pesticide residue left on food when the pesticide has been used according to label directions [22]. Because of this, the MRLs of the same active substance may vary depending on the country and climate. To support a more competitive crop trade strategy, the EU is investing in agricultural production within its member states to enhance food safety and nutritional value, while also fostering consumer confidence in food and agricultural products [23]. Effective pest management strategies and consumer health are ensured by the analysis of pesticide residue levels in food to identify the safe pre-harvest interval (PHI). PHIs and MRLs are both essential elements of good agricultural practices (GAP) compliance. The PHI refers to the time needed for pesticide concentrations to drop below the MRL after the last application of the pesticide [24].

While several studies have evaluated or optimized analytical methods for the determination of boscalid, estimated its residue levels, and assessed the dietary risk of boscalid in grapes and grape-based products [7,9], so far, research on dissipation kinetics studies under field conditions (evaluation and parametrization statistical models) of boscalid in table grapes are missing in the literature. Therefore, the current field study aims to (a) estimate the persistence, dissipation, and PHI of boscalid in two table-grape varieties (Soultanina and Crimson) in Northern Greece by applying three different kinetic models and to (b) quantify the pesticide exposure from table grape consumption and the associated health risks for both adults and children. In order to accomplish these objectives, table grape samples were analyzed using the QuEChERS sample preparation method followed by liquid chromatography combined with a diode array detector (HPLC-DAD).

2. Materials and Methods

2.1. Reagents and Chemicals

The analytical standards of boscalid, which had a 99.5 percent purity, were acquired by Dr. Ehrenstorfer GmbH in Augsburg, Germany. The HPLC grades, acetonitrile, water, methanol for stock solutions preparation, extraction and clean-up procedure, and instrumental analysis were obtained by Riedel de Haen (Seelze, Germany). Anhydrous magnesium sulfate, anhydrous sodium acetate, and NaCl (>99%) were obtained by Sigma-Aldrich Merck KGaA (Darmstadt, Germany). Agilent Technologies (Palo Alto, CA, USA) provided the bondesil carbon SPE sorbent and bondesil PSA (primary secondary amine). The spray solution was made with the pesticide Cantus[®] 50 WG (provided by Bayer Hellas A.G., Marousi, Greece), which has a 50% *w/v* boscalid content.

2.2. Experimental Set-Up

Field studies were conducted in the Kavala prefecture, Eastern Macedonia, and Thrace administrative region, in Northern Greece. The experimental setup included both a dissipation treatment area and a blank control, arranged in two experimental blocks. A buffer zone was established between plots, and the fields were separated into blocks of 30 m². Each block contained three replicates of each treatment, randomly assigned. The experiments for the two varieties of grapes were carried out in two separate fields following the same experimental design. To examine the trend of degradation and residues of boscalid in grapes, the commercial formulation of Cantus 50[®] WG was sprayed onto the surface of grapes at 120 g (a.i)/ha (recommended dose). Grapes were randomly collected from different directions and different parts of the cultivated area at 2 h (considered as the initial concentration), 2, 8, 16, 24, 28, and 36 (harvest day) days post-application of boscalid. The sample portion was more than three grape bunches (mature and disease-free with total weight approximately equal to 2 kg) from three experimental plots (three repetitions). Blank control grape samples were also collected. All samples were placed into plastic bags and transferred to the pesticide analysis laboratory within 8 h. Once in the lab grapes were collected from each plot, mixed, cut into small pieces, homogenized by a blender, split by quartering method for further analysis and stored at −20 °C until analysis.

2.3. Sample Preparation

At various intervals, random grape samples of 2 kg were taken from each experimental plot, in three replications. Following Parlakidis et al. [25], the QuEChERS analytical approach with slight modifications was applied. Aliquots of the homogenized material (10 g) were weighed into 50 mL PTFE centrifuge tubes in order to extract the boscalid. Each tube received 10 mL of acetonitrile, which was then mixed by vortexing for 2 min. The tube was then vortexed again for 1 min after adding 1 g of NaCl and 4 g of anhydrous MgSO₄. The resulting extracts were then centrifuged for 3 min at 4000 rpm. After filling 150 mg of anhydrous MgSO₄ and 50 mg of PSA to a 5 mL centrifuge tube, 1.5 mL of the upper acetonitrile phase was added as an aliquot. After the mix on vortex 1 min, the samples were centrifuged at 4000 rpm for 10 min. Prior to HPLC-DAD analysis, the supernatant of samples was filtered using a 0.45 µm Millipore filter (Eschborn, Germany) and transferred in HPLC vials.

2.4. HPLC Analysis

Similar to Parlakidis et al. [26], an autosampler-equipped HPLC–DAD chromatographic system was used to analyze the samples. The ChromQuest 5.0 program was used to analyze quantitative data. An autosampler-equipped HPLC–DAD chromatographic system (Finnigan Surveyor, Thermo Scientific, Waltham, MA, USA) was used to analyze

the samples. The Hypersil GOLD 100×4.6 mm analytical column (Fortis Technologies Ltd., Cheshire, UK) was protected by a Hypersil GOLD 10×4 mm precolumn and set at 25°C . The ChromQuest 5.0 program was used to analyze quantitative data. Acetonitrile (code name A) and water (code name W) formed the gradient mobile phase, which had a flow rate of 1.0 mL/min and phases of 20%–M/80%–W (0–10 min), 80%–A/20%–W (10–11 min), 95%–A/5%–W (11–25 min), and 20%–A/80%–W (26–30 min). The injection volume was established at $25\text{ }\mu\text{L}$, and the total run time analysis was 30 min. Data were taken at ultraviolet (UV) spectrum wavelengths of 235, 240, and 263.

2.5. Method Validation

Methanol was used to generate stock solutions of the boscalid at 100 mg/mL . To estimate the matrix effect, calibration standards in methanol and matrix-matched calibration standards were prepared. The linearity was assessed using the correlation coefficient of matrix-matched calibration curves considering five different concentrations. The linearity of the calibration curve in methanol was also tested using five concentrations. Prior to use, all of the standard solutions were stored in a refrigerator at -20°C .

The definition and evaluation of the accuracy/recovery, linearity and application range of calibration curve, the limit of detection/quantification (LOD/LOQ), and the matrix effect (ME) for Soultanina and Crimson grapes were determined according to European SANTE/11945/2015 Guidedance [27] and Parlakidis et al. [26]. Calibration curves were linear in the range of $0.1\text{--}5\text{ mg/mL}$, had a $R^2 > 0.99$ (correlation coefficient), and the retention time of boscalid was 11.81 min. Boscalid LOD and LOQ were 0.01 and $0.02\text{ }\mu\text{g/g}$, respectively. Recoveries ranged from 81 to 105% at all concentration ranges tested ($0.02\text{--}2\text{ }\mu\text{g/g}$), with RSD% values ranging from 5.93% to 19.275%. To identify a possible matrix effect, calibration curves made with standards in methanol were contrasted with those made with standards in grape matrix. The ME were mild in each case, ranging from -8.75 to -5.71 . Boscalid chromatographs are presented below (Figures 1 and 2).

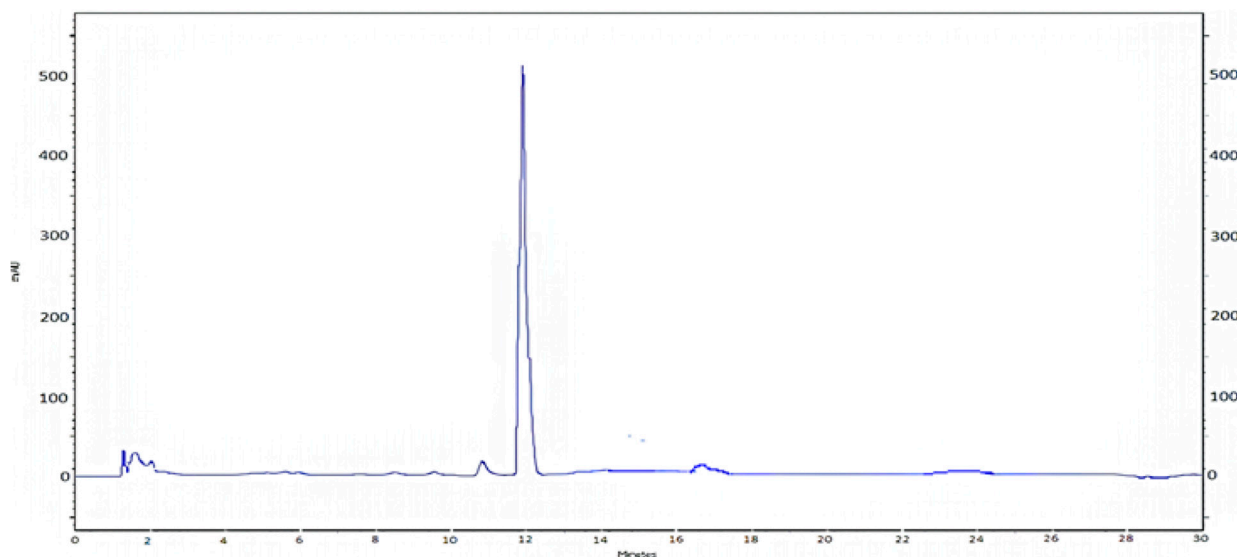


Figure 1. HPLC-DAD chromatographs of spiked Soultanina matrix with boscalid (0.020 mg/Kg). The retention time for boscalid is 11.81 min. In this HPLC-DAD chromatogram from ChromQuest 5.0, the x -axis represents the retention time in minutes, while the y -axis shows the absorbance in milli-Absorbance Units (mAU).

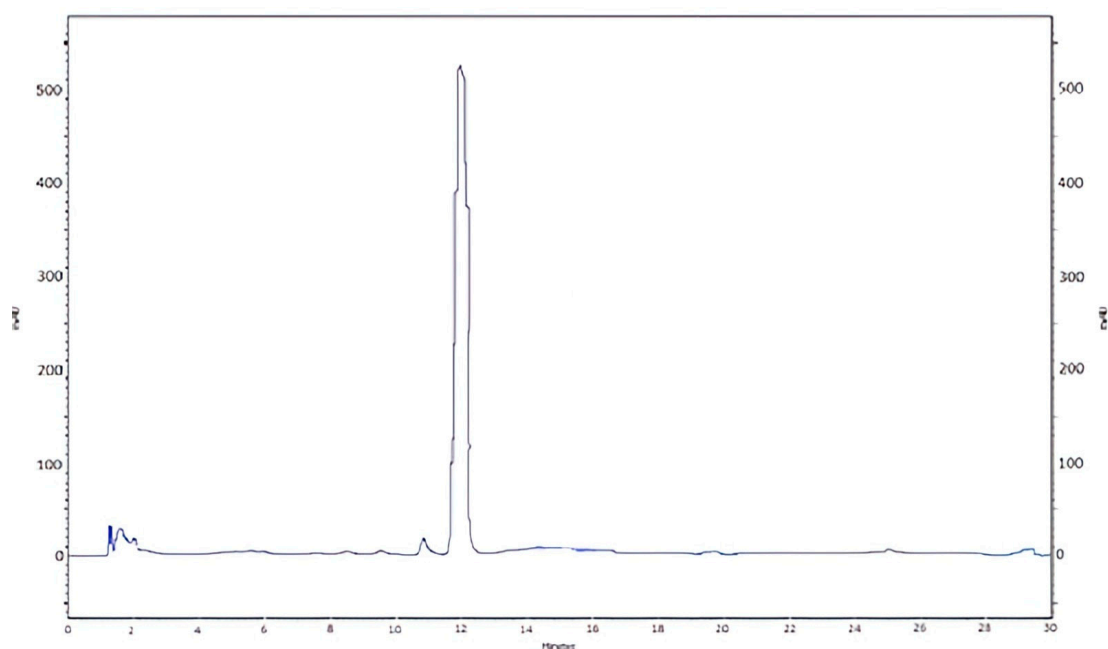


Figure 2. HPLC-DAD chromatographs of spiked Crimson matrix with boscalid (0.020 mg/Kg. The retention time for boscalid is 11.81 min. In this HPLC-DAD chromatogram from ChromQuest 5.0, the x -axis represents the retention time in minutes, while the y -axis shows the absorbance in milli-Absorbance Units (mAU).

2.6. Kinetic Models for Modeling of Dissipation

There are several kinetic models that describe the dissipation of pesticides with respect to time [28,29]. Among them, the zero-order, first-order, and second-order kinetic models were used in this work to predict the dissipation of boscalid in table grapes. These models are described by the following equations:

Zero-order (ZO) kinetic model.

$$C_t = C_0 - kt \quad (1)$$

$$DT_{50} = \frac{C_0}{2k} \quad (2)$$

$$DT_{90} = \frac{9C_0}{10k} \quad (3)$$

First-order (FO) kinetic model.

$$C_t = C_0 e^{-kt} \quad (4)$$

$$DT_{50} = \frac{\ln 2}{k} \quad (5)$$

$$DT_{90} = \frac{\ln 10}{k} \quad (6)$$

Second-order (SO) kinetic model.

$$C_t = \frac{C_0}{1 + C_0 kt} \quad (7)$$

$$DT_{50} = \frac{1}{C_0 k} \quad (8)$$

$$DT_{90} = \frac{9}{C_0 k} \quad (9)$$

where C_t ($\mu\text{g/g}$) is the pesticide concentration at time t (d), C_0 ($\mu\text{g/g}$) is the initial concentration at $t = 0$, k (1/day) is the dissipation rate constant, and DT_{50} (day) and DT_{90} (day) are the time required for the pesticide concentration to decrease by 50% and 90%, respectively.

The following statistical evaluation criteria were used to evaluate the performance of each kinetic model in predicting boscalid concentration by testing the agreement between predicted and measured value [30,31].

1. The use of scatterplots, where predicted values (P_i) are plotted against measured (or observed) values (O_i). In a scatterplot, a regression line of the form $P_i = \gamma O_i$ (where γ is the slope of the line) is fitted through the data, and the correlation coefficient R^2 is calculated. Model performance is acceptable when values for both the slope γ and R^2 are as close as possible to 1.0. There is an overestimation or underestimation of the model compared to the measured data for values of $\gamma > 1$ or $\gamma < 1$, respectively.

2. The root mean square error (RMSE) and the normalized objective function (NOF), which are calculated using the following equations:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^N (P_i - O_i)^2}{N}} \quad (10)$$

$$\text{NOF} = \frac{\text{RMSE}}{O_{\text{mean}}} \quad (11)$$

where O_{mean} is the mean of the measured values, and N is the total number of measurements. The ideal value of NOF is 0.0 and the acceptable value is between 0.0 and 1.0.

3. The Nash–Sutcliffe coefficient of efficiency (NSE), which is calculated using the following equation:

$$\text{NSE} = 1 - \frac{\sum_{i=1}^N (O_i - P_i)^2}{\sum_{i=1}^N (O_i - O_{\text{mean}})^2} \quad (12)$$

The best value for NSE is 1.0, but values between 0.75 and 1.0 indicate good agreement between predicted and measured values.

4. The mean absolute error (MAE), which is which is calculated with the following equation:

$$\text{MAE} = \frac{\sum_{i=1}^N |O_i - P_i|}{N} \quad (13)$$

All NSE and MAE model symbols are explained above. The optimum value of MAE is 0.0.

2.7. Evaluation of Risk Assessment

For the dietary risk assessment, the methodology described in the document *Principles and methods for the risk assessment of chemicals in food* (Environmental Health Criteria 240, WHO/IPCS, 2009) was selected, as applied by Golge and Kabak [9,32]. This framework is internationally recognized, developed jointly by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) and is widely applied in chemical risk assessments in food across different populations and regulatory contexts.

This approach was considered more appropriate than other available tools, such as EFSA's PRIMo (pesticide residue intake model), which is primarily designed for use within the European Union and includes consumption data for a limited number of EU member states. In the present study, national consumption data for grapes specific to the Greek population were used in order to assess dietary exposure and risk at a country-specific

level. Therefore, the IPCS methodology provided the necessary flexibility, allowing for the incorporation of local dietary patterns and the calculation of daily intake based on realistic consumption scenarios.

The risk assessment method evaluates potential exposure to pesticide residues to ensure that the acceptable daily intake (ADI) of the pesticides is not exceeded. As long as the pesticide residues consumed by individuals remains below the relevant ADI, consumers are considered to be adequately protected. Therefore, estimating human exposure to pesticides through the food supply and understanding the associated health risks becomes more straightforward [15]. Human health risk assessment was carried out according to Golge and Kabak [9] considering two age groups (children and adults), to estimate exposure levels and hazard quotient (HQ).

To estimate the risks to consumer health from boscalid residue in grapes, the long-term exposure was determined. The following equation was used to determine the exposure to boscalid residue:

$$\text{Exposure} = \frac{\text{mean concentration residue in grape} \times \text{grape consumption}}{\text{body weight}} \quad (14)$$

The Hellenic Statistical Authority provided the consumption data for the Greek populace, mentioning the average amount of table grapes consumed (i.e., 0.16 kg/person/day). For exposure estimation, EFSA recommends body weights of 70 kg for adults and 23 kg for children aged 3–10 years [33].

By dividing the exposure to that mean concentration residue by the ADI for that residue, the HQ for boscalid was determined. If the HQ is more than 1, the pesticide's ADI (i.e., 0.04 µg/g_{bw}/day) has been exceeded, and there may be a risk. Equation 15 displays the HQ calculation.

$$\text{HQ} = \frac{\text{exposure to boscalid}}{\text{ADI}} \quad (15)$$

3. Results and Discussion

3.1. Residues and Dissipation Kinetics of Boscalid in Table Grapes

The residue and dissipation kinetics of boscalid in grapes were examined under field conditions, with the fungicide applied at the recommended dose of 120 a.i./ha. Table 1 provides the detected residue of boscalid throughout the experiment along with the percentage of residue decline (%). The initial boscalid deposits in the grapes 2 h after application were 17.70 and 16.11 µg/g for Soultanina and Crimson varieties, respectively. After 2 days of application, boscalid had dissipated by 38.70% in Soultanina and 39.35% in Crimson. The residue continued to decrease progressively, with declines of 67.51% and 51.64% observed 8 days after application. From 8 days to 16 days, the dissipation rate of boscalid in two grape varieties was 79.60% and 72.87, respectively. From 16 to 24 days, residue declines were 87.57% and 86.03%, respectively. On day 28, the residue declines were 92.99% for Soultanina and 89.94% for Crimson.

The dissipation pattern of boscalid in Soultanina and Crimson varieties are shown in Figures 1 and 2, respectively. The dissipation rate of boscalid in both table-grape varieties is initially higher and then decreases over time indicating a non-linear pattern. This fact shows that zero-order kinetics is not suitable to explain the dissipation of boscalid in both Soultanina (Figure 3a) and Crimson variety (Figure 4a). In both varieties, the most suitable kinetics seem to be the FO and SO kinetic models (Figure 3b,c and Figure 4b,c), a fact that is also confirmed by the corresponding scattergrams with the values of the parameters γ and R^2 being approximately 1.0 (Table 2). Based on the other performance criteria (i.e., NOF, NSE, and MAE), it appears that the second-order kinetic model, with very little difference from the first-order one, better simulates the dissipation of boscalid in both table-grape

varieties (Table 2). More specifically, with optimal values of 0.0, 1.0, and 0.0 of the NOF, NSE and MAE criteria, respectively, the values for the Soultanina cultivar for FO and SO models were 0.23, 0.95, 0.98 and 0.11, 0.99, 0.49, respectively. The dissipation pattern of boscalid in the Crimson grape variety followed a similar non-linear trend as observed in the Soultanina variety, with an initially rapid decline followed by a slower dissipation rate over time. This behavior indicates that zero-order kinetics do not adequately describe the dissipation dynamics of boscalid in Crimson grapes. The first-order (FO) and second-order (SO) kinetic models both provided a good fit to the experimental data. The performance evaluation criteria supported this, with γ and R^2 values close to 1.0 and improved indicators across NOF, NSE, and MAE metrics. For the FO model, the values obtained for Crimson were $\gamma = 1.030$, $R^2 = 0.9438$, NOF = 0.2546, NSE = 0.9219, and MAE = 1.100. For the SO model, the corresponding values were $\gamma = 0.953$, $R^2 = 0.943$, NOF = 0.213, NSE = 0.9404, and MAE = 0.910. These results suggest that although both FO and SO models are suitable, the SO model slightly outperforms the FO model in describing the dissipation kinetics of boscalid in the Crimson variety. (Table 2).

Table 1. Residue and dissipation rate of boscalid in Soultanina and Crimson varieties.

Days After Application	Soultanina		Crimson	
	Residue ($\mu\text{g/g}$) ¹	Residue Decline (%)	Residue ($\mu\text{g/g}$) ¹	Residue Decline (%)
0 (2 h)	17.70 (± 2.79)	-	16.11 (± 1.58)	-
2	10.85 (± 1.58)	38.70	9.77 (± 0.63)	39.35
8	5.75 (± 1.09)	67.51	7.79 (± 0.42)	51.64
16	3.61 (± 1.06)	79.60	4.37 (± 0.38)	72.87
24	2.20 (± 0.80)	87.57	2.25 (± 0.39)	86.03
28	1.24 (± 0.39)	92.99	1.62 (± 0.40)	89.94
36	0.11 (± 0.02)	99.38	0.23 (± 0.10)	98.57

¹ mean concentration of three replications; the number in bracket indicates the standard deviation.

Table 2. Performance evaluation criteria of three kinetic models fitted to dissipation of boscalid in table grapes.

Model Kinetic	Performance Criteria	Table-Grape Variety	
		Soultanina	Crimson
Zero order	¹ γ	1.26	1.25
	² R^2	0.66	0.76
	³ NOF	0.67	0.51
	⁴ NSE	0.54	0.65
	⁵ MAE	2.8	2.34
First order	γ	1.04	1.03
	R^2	0.96	0.94
	NOF	0.23	0.25
	NSE	0.95	0.92
	MAE	0.983	1.100
Second order	γ	0.99	0.95
	R^2	0.99	0.94
	NOF	0.11	0.21
	NSE	0.99	0.940
	MAE	0.49	0.91

¹ slope, ² correlation coefficient, ³ normalized objective function, ⁴ root mean square error, ⁵ mean absolute error.

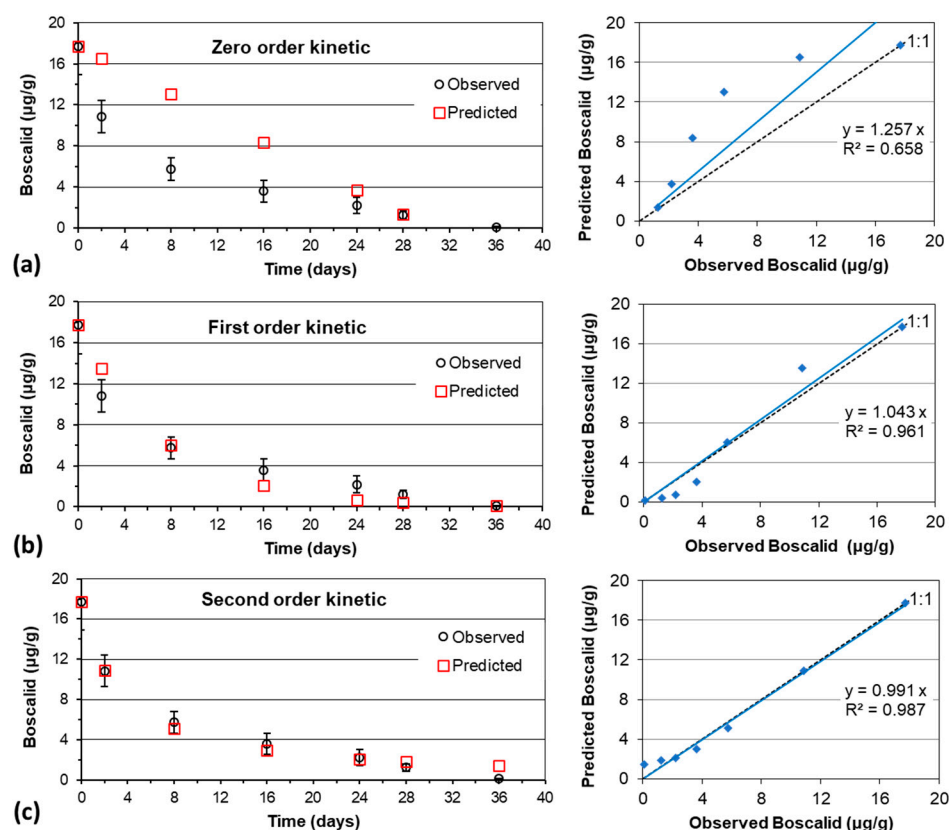


Figure 3. Dissipation trend (left) of boscalid in Sultana grape and scatterplots (right) of measured vs. predicted boscalid concentrations for kinetic model: (a) zero order; (b) first order; (c) second order. Error bars represent the standard deviation.

The SO model has also been utilized by the majority of researchers to forecast how boscalid will dissipate differently in different types of plants [34–38]. According to Torabi et al. [29], the application of the SO provided satisfactory goodness-of-fit indices for the dissipation dynamics prediction of neonicotinoids and abamectin in pistachio nuts.

The log-linear models FO and SO view pesticide dissipation as a single-phase process with a single rate constant with and a stable dissipation rate in grapes [39], as demonstrated in our study. In contrast, bi-exponential models comprise two basic first-order kinetics. The initial concentration of a pesticide is assumed to be split between two fast- and slow-degrading phases. The initial concentration of a pesticide that is easily accessible to the enzymes that break it down in the solution phase quickly disappears. After reaching a dynamic equilibrium, the leftover portion, which may be absorbed by the plant tissue particles, breaks down gradually [29].

Table 3 shows the dissipation parameters of boscalid in the two table-grape varieties, which were calculated with the three kinetic models (i.e., ZO, FO, and SO). As mentioned above, more reliable are the results obtained from the application of the FO and SO kinetic models. The application of the ZO does not comply with statistical indices criteria.

For the Sultana variety, the boscalid half-lives were 5.14 and 3.32 days, and the DT_{90} were 17.05 and 29.87 days for the FO and SO models, respectively. For Crimson variety, the boscalid half-lives were 6.42 and 3.65 days, and the DT_{90} were 21.32 and 32.86 days for the FO and SO models, respectively. These results show that the degradation of boscalid occurs slightly faster in the Sultana variety compared to the Crimson one.

Azoxystrobin and other high-molecular weight substances break down slowly, while boscalid and other low-molecular weight compounds break down more quickly. The penetration of pesticides, particularly those soluble in water, may be hindered by the

wax coating that covers the surface of certain plants [10,38]. Also, it is anticipated that hydrophobic chemicals will readily permeate and accumulate in the wax layer, similar to that found in fatty animal tissue [39].

Table 3. Dissipation kinetic parameters of boscalid in two table-grape varieties.

Parameters	Table-Grape Variety	
	Soultanina	Crimson
Zero-order model (ZO): $C = C_0 - kt$		
Kinetic equation	$C = 17.72 - 0.585t$	$C = 16.11 - 0.495t$
k (1/day)	0.59	0.50
DT ₅₀ (days)	15.14	16.30
DT ₉₀ (days)	27.26	29.30
First-order model (FO): $\ln C = \ln C_0 - kt$		
Kinetic equation	$\ln C = \ln 17.72 - 0.135t$	$\ln C = \ln 16.11 - 0.108t$
k (1/day)	0.14	0.11
DT ₅₀ (days)	5.14	6.42
DT ₉₀ (days)	17.05	21.32
PHI (days)	9.37	10.90
Second-order model (SO): $C = C_0 / (1 + C_0 kt)$		
Kinetic equation	$C = 17.72 / (1 + 0.301t)$	$C = 16.11 / (1 + 0.274t)$
k (1/day)	0.02	0.02
DT ₅₀ (days)	3.32	3.65
DT ₉₀ (days)	29.87	32.86
PHI (days)	8.45	8.11

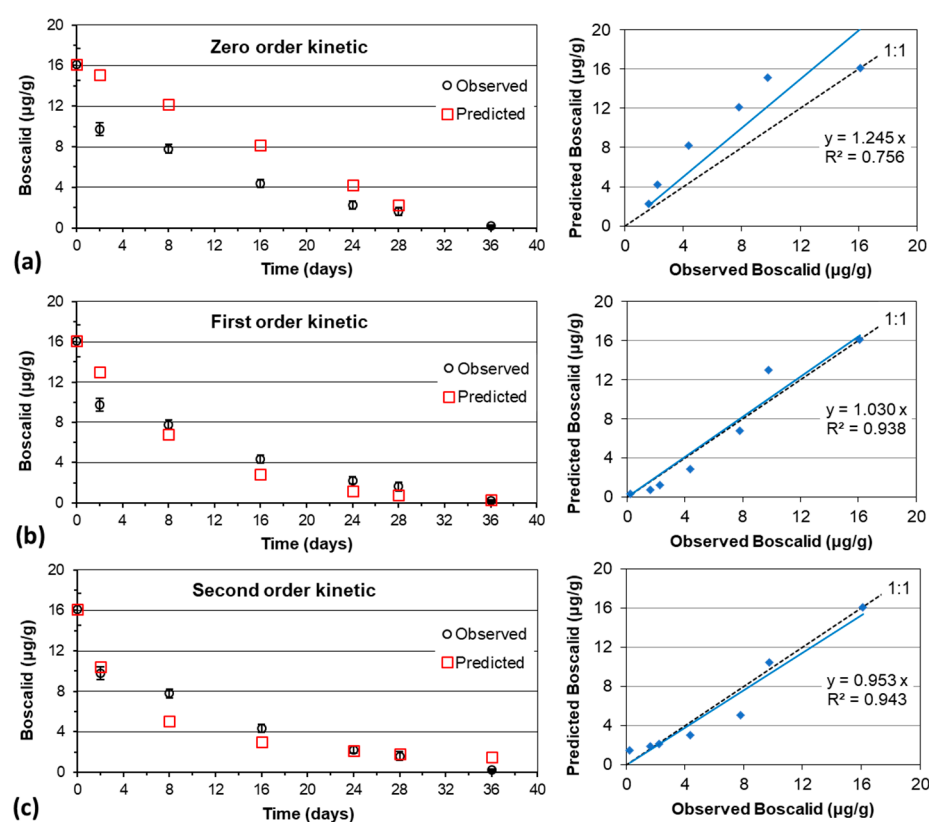


Figure 4. Dissipation trend (left) of boscalid in Crimson grape and scatterplots (right) of measured vs. predicted boscalid concentrations for kinetic model: (a) zero order; (b) first order; (c) second order. Error bars represent the standard deviation.

It has been observed that the half-lives of boscalid varied depending on the substrate (fruits, vegetables, soil) [31]. According to Munitz et al. [40], boscalid in fruits from the Emerald and Jewel cultivars had a half-life of 5.3 and 6.3 days, respectively. However, Jankowska et al. [41] and Wolejko et al. [38] observed a DT_{50} of 3.09 and 3.2 days for tomatoes and lettuce, respectively, while Sadlo et al. [42] estimated a DT_{50} of 7 days for boscalid in raspberry fruit. Additionally, boscalid was found to have a half-life of 9.8 days in ripe apples and 4.9 to 6.4 days in strawberries [43,44]. He et al. [34] noted, for example, that the retention of boscalid in soil and plants differed significantly with cucumber dissipation and was 3 times faster than soil dissipation.

Therefore, the different degradation rates may be associated to crops varieties as well [35,44]. The residue in Soultanina and Crimson grapes were different, suggesting that pesticide residues are influenced by the fruit's properties. As a result, when using pesticides, an appropriate utilization plan should be created based on the real circumstances [32].

Climate variables could be responsible for the variations in the dissipation behavior of these various substrates. According to previous studies, pesticides will dissipate more quickly in warm, humid conditions, and heavy rains will significantly raise the possibility of most compounds running off into the soil and favor the leaching of various pesticides. High temperatures and prolonged sunshine will also encourage the breakdown and volatilization of pesticides [45]. Higher temperatures can also encourage the growth of microorganisms and, to some extent, hasten the environment's breakdown of pesticides [40,43,46]. High precipitation can also accelerate acidity and affect how pesticides decomposed [46]. Given that Northern Greece is located in the Mediterranean climate zone, its higher temperatures and copious amounts of precipitation may result in a different rate of pesticide dissipation than other regions, as studies showed previously [26,46,47].

According to Paramasivam [48] and Torabi et al. [49], plotting residue versus time and applying MRL ($5 \mu\text{g/g}$) established by EU [50] and the rate constant obtained from kinetic equations, PHI was found. The PHI for 120 g a.i./ha was determined for Soultanina and Crimson to be 9.37 and 10.90 days, respectively, for the FO model and 8.45 and 8.11 days, respectively, for the SO model (Table 3). The aforementioned data showed that the residue of boscalid were decreased below the MRL (i.e., $5 \mu\text{g/g}$) that is considered acceptable. As a result, Soultanina and Crimson grape varieties could be consumed with low risk.

The PHI, defined as the time between the last pesticide application and crop harvest, plays a pivotal role in determining the final residue levels found in food commodities. In our study, the residue concentrations measured at the specified PHI align with the median levels reported in supervised trials, underlining the critical role of appropriate PHI adherence in ensuring compliance with maximum residue limits (MRLs). Short PHIs may not allow sufficient time for the degradation of pesticide residues, thereby increasing the likelihood of dietary exposure, particularly among sensitive subpopulations such as children [51].

3.2. Dietary Risk Assessment

For the purpose of determining the long-term dietary risk assessment of Cantus® 50 WG applied to two grape varieties grown under field conditions, residue dissipation results were utilized. Both adults and children between the ages of 3 and 10 made up the consumer groups for which the exposure and the HQ were calculated. If the HQ was more than 1, the pesticide's ADI had been exceeded and there may have been a risk.

Regarding Soultanina consumption safety, the exposure ranged from 0.12 to $1.0 \times 10^{-3} \mu\text{g/g}_{\text{bw}}/\text{day}$ and from 0.04 to $0.00 \mu\text{g/g}_{\text{bw}}/\text{day}$ for children and adults, respectively (Table 4). More than unity HQ values from 0 (2 h), 2, and 8 days after the

application of boscalid were determined for children, while adults are under high risk only 2 h after the boscalid spray (Table 4).

Table 4. Dietary and risk assessment of boscalid in Soultanina and Crimson at 120 g.a.i./ha.

Table Grape	Days After Application	Children		Adults	
		Exposure ($\mu\text{g}/\text{g}_{\text{bw}}$ ¹ day)	HQ ²	Exposure ($\mu\text{g}/\text{g}_{\text{bw}}/\text{day}$)	HQ
Soultanina	0 (2 h)	0.12	3.10	0.04	1.02
	2	0.09	1.90	0.03	0.62
	8	0.04	1.01	0.01	0.33
	16	0.03	0.63	0.01	0.21
	24	0.02	0.39	0.01	0.13
	28	0.01	0.22	3.0×10^{-3}	0.07
	36	1.0×10^{-3}	0.02	0.00	0.01
Crimson	0 (2 h)	0.11	2.82	0.04	0.93
	2	0.07	1.71	0.02	0.56
	8	0.06	1.36	0.02	0.45
	16	0.03	0.76	0.01	0.25
	24	0.02	0.39	0.01	0.13
	28	0.01	0.28	4.0×10^{-3}	0.09
	36	2.0×10^{-3}	0.04	1.0×10^{-3}	0.01

¹ Hazard Quotient; ² bw.

Children and adults' exposure to boscalid through Crimson grapes consumption ranged from 0.11 to 2.0×10^{-3} $\mu\text{g}/\text{g}_{\text{bw}}/\text{day}$ and from 0.04 to 1.0×10^{-3} $\mu\text{g}/\text{g}_{\text{bw}}/\text{day}$, respectively (Table 4). The HQ values were not greater than unity after 16, 24, 28, and 32 days after the fungicide application for both children and adults, indicating that the consumption of grapes is safe. However, the consumption of grapes could pose a risk after 2 h, 2, and 8 days after the application of boscalid for children. During the first 36 days, adult consumers have a low risk (Table 4).

In view of recent risk assessment studies, like the one conducted by Zhao et al. [52], which assessed chronic dietary exposure to pyraclostrobin and cyazofamid across various population groups, the findings of our investigation regarding pesticide residues in grapes become even more significant. The study found that the median residue levels of cyazofamid and pyraclostrobin in grapes were 0.11 and 0.13 mg/kg, respectively. The authors showed that regional dietary patterns and increased grape consumption per body weight are the primary causes of chronic dietary risk in some situations, particularly for children.

4. Conclusions

This study assessed the dissipation kinetics and dietary risk of boscalid residue in two widely cultivated table-grape varieties, Soultanina and Crimson, under field conditions in Northern Greece. The dissipation of boscalid followed a non-linear trend, with both first-order (FO) and second-order (SO) kinetic models providing a good fit to the experimental data. Based on statistical performance indices (γ , R^2 , NOF, NSE, MAE), the SO model slightly outperformed the FO model, reflecting a more accurate simulation of boscalid degradation in both grape varieties. The calculated half-lives (DT_{50}) ranged between 3.32 and 6.42 days, while the DT_{90} values ranged between 17.05 and 32.86 days. The pre-harvest intervals (PHIs), estimated using kinetic parameters and the European MRL threshold (5 $\mu\text{g}/\text{g}$), were between 8.11 and 10.90 days, ensuring compliance with regulatory safety standards.

Dietary risk assessment, conducted using grape consumption data specific to the Greek population, revealed that children are more vulnerable to pesticide exposure than

adults, with HQ values exceeding unity during the early post-application period. This heightened risk is attributed to higher consumption of grapes per unit body weight. The study underscores the importance of adhering to recommended PHIs to secure consumer health, particularly in vulnerable populations such as children.

In conclusion, the results of this study provide valuable data for risk managers, growers, and regulatory authorities. They support evidence-based decisions regarding safe use practices of boscalid in table grapes, while also emphasizing the importance of integrating kinetic modeling and realistic exposure scenarios into pesticide risk assessment frameworks.

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